Directly absorbing Therminol-Al_2O_3 nano heat transfer fluid for linear solar concentrating collectors

M. Muraleedharan[1], H. Singh[2*], S. Suresh[1], M. Udayakumar[1]

[1]Department of Mechanical Engineering, National Institute of Technology, Tiruchirappalli, 620015, India
[2] Institute of Energy Futures, Brunel University London, Kingston Lane, Uxbridge, UB8 3PH, UK

[*] Corresponding author Email: harjit.singh@brunel.ac.uk; Tel: +44-(0)20-87514442

Abstract

This paper reports experimentally measured thermal and optical properties of Al_2O_3 - Therminol®55 nano heat transfer fluid (nHTF) in conjunction with a specially developed line focussing Fresnel lens based solar thermal concentrator. Solar collector tests were conducted under real life outdoor ambient and solar radiation conditions. A range of volumetric proportions of Al_2O_3 (0.025 vol% - 0.3 vol%) have been covered. Highest thermal conductivity and refractive index were measured for nHTF with 0.1 vol% concentration of Al_2O_3 with higher concentrations (>0.1 vol%) concluded to be unfit for their use in the solar collector applications due to likely agglomeration and sedimentation in the hours of low or nil sunshine when fluid is not circulating. Thermal conductivity enhanced by 11.7% for 0.1 vol% Al_2O_3 concentration nHTF. A highest temperature of 132.8 °C was delivered by the solar collector using 0.1% concentration Al_2O_3 nHTF at a flow rate of 0.5lps. This was 44.7 °C higher than that achieved by pure Therminol®55 (88.1 °C) even though the DNI during 0.1% nHTF test was considerably lower than that for the later. The solar concentrator thermal efficiency increased with the proportion of NPs attaining a maximum of 52.2% for 0.1vol% Al_2O_3 nHTF. Directly absorbing nHTFs along with the solar collector developed in this study are predicted to be strong candidate to replace conventional metallic tube receiver using concentrators due to advantages of size compaction and higher thermal conversion efficiency.

Keywords: Therminol-55, Alumina (Al_2O_3) nanoparticles, Nano heat transfer fluid, Thermal conductivity, Zeta potential, specific heat, refractive index, Concentrating solar collector, Linear Fresnel lens.

1. Introduction

Thermal, flow and optical properties of nHTFs are of particular interest due to their potential use as directly absorbing working fluid in solar collectors. Dispersion of nanoparticles (NPs) in conventional heat transfer fluids has been shown to improve their thermal properties, for example, references [1-3]. Chandrasekar et al. [2] experimentally measured thermal conductivity of Al_2O_3-water nHTF, for NP concentration varying from 0.33 vol% to 5 vol%, to be higher than that of water. Sani et al. [4] reported optical characterisation of nHTF comprising single-wall carbon nano horns and ethylene glycol. Hordy et al. [5] studied stability of plasma functionalized multi-walled carbon nanotubes suspension in ethylene glycol and propylene glycol at 170 °C for 8 months. Agglomeration was found to occur in non-polar Therminol VP-1 heat transfer fluid. Gupta et al. [6] reported a 39.6% rise in instantaneous efficiency for a flat plate solar collector when directly absorbing Al_2O_3-water nHTF nanofluid with 20 nm Al_2O_3 nanoparticles 0.005 vol% was used. A clear optimum volume faction of 0.005% was observed due to a concomitant increase in heat loss as the solar absorption increased. Taylor et al. [7] described modelling and experimental methods to determine the optical properties of nHTFs. Khullar et al. [8] theoretically predicted a 5–10% higher efficiency for a parabolic concentrator using nHTF consisting of spherical aluminium NPs suspended in Therminol VP-1 than a conventional parabolic solar collector. Anoop et al. [9] reported a rise in refractive index by <1% with an increase in nanoparticle loadings in SiO_2 - water nHTF. Said et al. [10, 11] investigated the effect of size and concentration of TiO_2 NPs on optical properties of nHTF. The size of NPs (TiO_2 and Al_2O_3) was found to have a nominal effect on optical properties of water based nHTFs while the extinction coefficient increased linearly with increase in volumetric concentration. Also, it was found that TiO_2 had better optical properties than Al_2O_3, but it formed a less stable suspension in water than the later. Thermo-physical characterisation of Therminol®55 based nHTFs containing MgO NPs [12] and CuO NPs [13] have also been reported.

This paper reports the results of an experimental investigations ino the suitability of Al_2O_3- Therminol® 55 based nHTF as directly absorbing working fluid for solar thermal concentrating collectors. Therminol®55 was preferred because of its stable physical and thermal properties over the temperature rage of interest, ≤200°C, and Al_2O_3 for superior thermal and optical properties. To the best of authors' knowledge, this is the first study reporting experimentally measured thermal, physical and optical characteristics of Al_2O_3-Therminol®55 nHTF and its real life performance as directly absorbing working fluid in a line axis solar concentrating collector comprising linear Fresnel lens.

2. Experimental details

2.1 nHTF preparation

Fig.1 shows the methodology adopted for the preparation of alumina (Al_2O_3)-Therminol®55 nHTF and its characterization. Commercially available spherical Al_2O_3 [14] nanoparticles with 99.5% purity (refractive index of 1.768 and surface area 32-40 m^2/g) were used to prepare nHTF. Surface morphology and microstructure of the nano particles was observed using a scanning electron microscope. SEM images of alumina at 200,00x and 30,00x are shown in Fig. 2. Images showed the spherical shape of alumina nanoparticles with an average size of 30 to 40 nm.

Therminol-55 [15] was used as the base fluid and Oleic acid [16] as surfactant because of its good miscibility and comparative viscosity with Therminol®55. The amount of nanoparticles added to the base fluid to achieve a particular volumetric concentration (ϕ) was calculated using equation (1).

$$\phi = \frac{W_{np}/\rho_{np}}{W_{np}/\rho_{np}+W_{bf}/\rho_{bf}} \qquad (1)$$

Where

W_{np} is the mass of NPs

ρ_{np} is the density of NPs

W_{bf} is the mass of base fluid

ρ_{bf} is density of base fluid

Mixture containing 0.5 mL of oleic acid per gram of Al_2O_3 NPs was first prepared [11] and dispersed into Therminol®55 using a magnetic stirrer for 45 minutes. Further to improve the stability of the nHTF sonication was done using an ultrasonic bath for 45 minutes. This procedure was followed to prepare samples of nHTF containing different volumetric concentrations of Al_2O_3, 0.025 vol%, 0.05 vol%, 0.075 vol%, 0.1 vol%, 0.2 vol% and 0.3 vol%. Fig. 3 shows samples of the nHTFs prepared with the fluid colour getting

paler as the concentration of NPs increased. Table 1 details the amount of Al_2O_3 and oleic acid used to prepare the nHTFs employed in the study.

2.2 Characterization of Al_2O_3–Therminol®55 nHTF

Stability of the nHTF samples was determined through measuring Zeta potential of nHTFs. Zeta potential is the physical property exhibited by any particle in suspension and is the electrostatic attraction or repulsion between the surface of the solid particle immersed in a conducting liquid and the bulk of the liquid. Zetasizer Nano ZS equipment [17], shown in Fig. 4a, was used to measure zeta potential. It is a high performance two angle particle and molecular size analyser for enhanced detection of aggregates and measurement of small or dilute samples and samples at very high or low concentration. Large zeta potentials either positive or negative indicate more stable dispersion. The thermal conductivity of the samples was measured using KD2 Pro Thermal Properties Analyser [18] shown in Fig. 4b. The absorbance of the nHTF was measured using UV-Vis spectrophotometer [19], Fig. 4c, for 400nm to 900nm wavelength at 25°C. It is a double beam spectrophotometer in which one beam passes through the sample and the other through the reference sample, and it quantitatively compares the amount of light passing through the test and reference sample.

Refractive index, an important parameter pertaining the nHTFs used as directly absorbing working fluids, such as those developed in this study, was measured using a Rudolph Research - J257 refract metre [18], Fig. 4d, for a wavelength of 589.3nm at 25°C. Water with a refractive index of 1.333 was taken as a reference sample. The specifications of the characterization instruments are detailed in Table 2.

2.3 Performance of nHTF in line-axis solar concentrator

The directly absorbing nHTFs was tested under real life outdoor conditions using a concentrating solar collector system specifically developed for this purpose during the study. The concentrator comprised four flat line-axis Fresnel lenses focusing visible solar radiation at four evacuated glass receiver tubes, a single-axis tracking system and a storage tank as shown in Fig. 5. Lens and receiver tube details are provided in Table 3. The collector was held in true North-South direction (surface azimuth angle 0°) and tracked about this axis to follow the movement of sun along East-West axis.

The receiver tubes consisted of an outer glass tube (external diameter 25 mm) surrounding an inner glass tube (internal diameter 10mm). The annular space between the outer and inner tubes was evacuated to a low air pressure of 10^{-3} mbar to suppress the convective heat loss from the warmer nHTF flowing through the internal tube to the surroundings. The four receiver tubes were located parallel to each other with each positioned directly below a Fresnel lens in such a way that the central long axis of a tube fell exactly on the focal line of the corresponding Fresnel lens just above it. The solar concentrator developed during the study is shown in Fig 6 with Fig. 6a showing the concentrator being tested outdoors and Fig 6b an illuminated receiver tube containing nHTF. Receiver tubes were connected in series such as the nHTF flows from one tube to another through an insulated flexible hose, see Fig. 5 and Fig 6(a). Global and diffused radiation were measured using pyranometers, one located in the shade and other directly on the inlet aperture plane of Fresnel lenses.

The Fresnel lens and receiver tubes were supported by an aluminium box frame and the Fresnel lenses and the receiver tubes assembly were tracked by a single axis tracking system. During testing the directly absorbing nHTF was pumped into the Fresnel lens concentrator at a constant flow rate of 0.5 lps using a rotameter and two control valves as shown in Fig. 5. Four calibrated k-type thermocouples (accuracy ±0.5 C) were deployed at the outlet of each receiver to measure nHTF temperatures.

3. Results and Discussions

3.1 Stability analysis by zeta potential test

Quantitative stability of Al_2O_3-Therminol®55 nHTFs prepared during the study was determined using zeta potential test. All the characteristic studies were carried out one week after the sample preparation. The sample with 0.025 vol% Al_2O_3 returned the highest zeta potential value of 52.4 mV; the zeta potential values reduced with an increase in Al_2O_3 concentration. Fig.7 shows the zeta potential distribution curve of 0.1 vol% concentration with Table 4 detailing the zeta potential values measured for the full range of the nHTFs studied.

It can be seen in Table 4 that an increase in the volumetric concentration of Al_2O_3 decrased zeta potential from 52.4 for 0.025 vol% to 24.8 for 0.3 vol%. A moderate fall in the stability of nHTF from 0.025 vol% till 0.1 vol% and a significant fall for concentrations >0.1 vol%

can be seen. This behaviour can be attributed to the potential NPs agglomeration leading to settling down of Al_2O_3 in the solution as the NP concenration increases.

3.2 Thermal conductivity

The addition of nanoparticles enhanced the thermal conductivity of Therminol®55 nHTF even at a low loading of 0.025 vol% concentration of Al_2O_3. Measured thermal conductivity values for the nHTFs over a full range of volumetric concentrations of Al_2O_3 in Therminol®55 are shown in Fig. 8. A clear maxima in thermal conductivity values was observed for nHTF with 0.1 vol% Al_2O_3. It achieved a maximum enhancement of 11.7% with an Al_2O_3 concentration of 0.1 vol%. Improvement in thermal conductivity was attributed to Brownian motion, nanoparticles clustering and liquid layering at liquid-nanoparticle interface. A drop in the thermal conductivity values was observed for Al_2O_3 concentrations of 0.2 vol% and 0.3 vol%, which is attributed to increased agglomeration at these concentrations. The increased agglomeration at higher concentrations was also indicated by lower zeta potential values, see Table 4.

3.3 Refractive index

Refractive indices for the nHTFs were measured at the optical wavelength of 589.3 nm at 25°C, see Fig. 8. The refractive index of alumina NPs employed is 1.768. The refractive index of Therminol®55 was measured to be 1.4858 and that of the nHTF with 0.025 vol % Al_2O_3 1.48607, indicating a rapid rise due to the presence of NPs. A further increase in the concentration of NPs increased the refractive index, though gradually, up to an Al_2O_3 concentration of 0.1 vol% beyond which (for 0.2 vol% and 0.3 vol% concentrations) refractive index decreased, a trend attributed to increased agglomeration of NPs.

3.4 Absorbance

Fig. 9 shows the measured absorbance spectra of the Al_2O_3-Therminol®55 nHTFs over the wavelength range of 400-900 nm at 25° C. Absorbance increased with an increase in the concentration of Al_2O_3 NPs due to direct absorption of electromagnetic radiation by the nanoparticles. Increase in the Al_2O_3 concentration resulted into a clear increase in the absorbance values. Also the point of maximum absorbance shifted towards right (to a higher wavelength) as the volumetric concentration of Al_2O_3 was increased, see fig. 9. The maximum absorbance for nHTF with 0.025 vol% was measured at 410nm, for 0.05 vol% at 444nm, for 0.075 vol% at 459nm and for 0.1 vol% at 501nm.

3.5 Testing of directly absorbing nHTF as working fluid in line-focussing solar concentrating collector

The developed solar collector, shown in Fig. 6a was tested outdoor under real life ambient and solar conditions at National Institute of Technology, Tiruchirappalli (India), using nHTFs synthesised containing Al_2O_3 in the concentrations of 0.025 vol%, 0.05 vol%, 0.075 vol% and 0.1 vol%. Decision to use nHTFs with Al_2O_3 concentration of ≤0.1 vol% was based on thermal conductivity, suspension stability and optical measurements described in the previous sections. During each test nHTF temperature at the outlet of each receiver tube and solar radiation intensity (global and diffuse) were measured. Tests were performed on comparatively sunnier days during the months of April to June 2016. The flow rate of the working fluid during all experiments was maintained at 0.5 lpm and measured using a rotameter. Experimental data was acquired using a data logger, Keysight 34972.

3.5.1 Direct normal incidence (DNI) radiation at the inlet apertur of the concentrator

One pyranometer was employed to measure the tilted (on Fresnel lens inlet aperture plane) global radiation and other for horizontal diffuse solar radiation during the full duration of the project. Using the measured global and diffuse radiation, DNI incident at the tilted inlet aperture of the solar collector was calculated employing the Maxwell Direct Insolation Simulation Code model [21]. The resulting DNI for the specific hours of testing is shown in Fig.10. Instead of giving the specific dates for which this data was calculated for, we have specified the nHTF to which any DNI curve corresponds. This is done to enable the reader to easily relate the data among various figures. It’s clear from fig. 10 that among all the test days, the least sunny was the one on which the tests were run for nHTF containing 0.1% concentration of Al_2O_3. The other days were more or less similarly sunny.

3.5.2 Thermal performance of the solar collector system

The instantaneous temperatures at the outlets of the solar collector receiver tubes recorded at half hourly intervals are shown in Fig. 11. These were recorded at the outlet of the fourth receiver tube from where the nHTF flows into the storage tank. Temperature of nHTF increased with a rise in Al_2O_3 NP concentration even though the solar DNI intensity at any half hourly interval remained nearly the same during testing, see Fig.10. It is concluded that the presence of Al_2O_3 NPs increased the solar radiation absorption due to high absorptivity and refractive index, see Fig. 8 and Fig. 9, and also that the absorbed radiation was converted into thermal energy, which was responsible for the temperature rise in nHTF. The highest temperature of 132.8 °C was achieved at 13:00 pm by the 0.1 vol% nHTF, 44.7 °C higher than that achieved by pure Therminol®55 fluid (88.1 °C) even though the DNI during 0.1 vol% nHTF test was lower than that for pure Therminol®55. Temperatures achieved at half hourly intervals for different nHTFs can be seen from Fig.11 with Fig.10 showing the DNI incident at the Fresnel lens inlet aperture.

Net energy gain delivered by the solar collector (Q_u) was calculated by using equation (2) employing the storage tank temperatures recorded before and after the experiment for every half hour.

$$Q_u = m_{sto} c_p \left(T_{sto,f} - T_{sto,i}\right) \quad (2)$$

Where

m_{sto} is the mass of nHTF in the storage tank

c_p is the specific heat of nHTF

$T_{sto,i}$ is the temperature of nHTF in the storage tank at the beginning of every half hour interval

$T_{sto,f}$ is the temperature of nHTF in the storage tank after every half hour interval

Thermo-physical properties such as specific heat (c_p) and density (ρ) of nanofluids consisting of various permutations of nanoparticles and Therminol®55 were computed by applying a parallel mixture rule for an effective property (P), shown in equation 3 (Khullar et al., 2012; Chandrasekar et al., 2009).

$$P = f_v P_{np} + (1 - f_v) P_{bf} \quad (3)$$

where

f_v is the volumetric fraction of the nanoparticles in the nHTF

P_{np} is the property of the nanoparticles (Al_2O_3)

P_{bf} is the property of the base fluid (Therminol®55)

Due to a low concentration of nanoparticles (0.025 vol% - 0.1vol%) dispersed in the base fluid, Therminol®55, these marginally affected base fluid properties, such as mass density and specific heat, at any given temperature, see fig. 12 for mass density and table 5 for specific heat.

Thermal loss from the solar collector components such as radiative loss from receiver tubes and radiative and convective heat loss from the storage tank and connecting hose were calculated using the expression (4).

$$\varepsilon\sigma A\left(T^4 - {T_s}^4\right) + hA(T - T_a) \quad (4)$$

where

ε is the radiative emissivity of the solar collector component, storage tank, hose, glass receiver tube or working fluid

σ is the Stefan Boltzmann constant

A is the relevant area of heat transfer of the component

h is the convective heat transfer between the solar collector component and ambient

T is the temperature of the component

T_s is the sky temperature

T_a is the ambient temperature

Radiative emissivity for the collector components was assumed to be constant with temperature. For example, for glass receiver tube the emissivity was assumed to have a constant value of 0.9 (Duffie & Beckman, 2006) and polyethylene hose 0.1. The storage tank (300mm diameter, 400mm high) was insulated with 50mm thick glass wool insulation (thermal conductivity 0.04 W/m.K). Radiative loss from nHTF contained in glass receiver tube was calculated assuming the inner glass tube surface temperature to be equal to that of the nHTF at any instant. No low emissivity coatings were employed in the glass tubes employed for the experiment. Any convective loss from the inner glass tube to the outer was neglected due to a low vacuum pressure maintained in the annulus between inner and outer tube. This was verified by measuring the surface temperature of the outer glass tube which remained within 1°C of the ambient temperature all through the experiments. Any conductive or radiative loss from the tank to ground loss were neglected. Any radiative loss from the insulated polyethylene tube connecting the glass receiver tubes and the tank was neglected.

Convective loss coefficient (h) from connecting hose (total length 3m) and storage tank to surrounding air was calculated using equation 5 (Duffie & Beckman, 2006).

$$Nu = \frac{h.D}{k} = 0.4 + 0.54Re^{0.52} \quad (5)$$

where

Re is the Reynolds number

D is the diameter

k is the thermal conductivity of surrounding air

The solar concentrator thermal efficiency was calculated as the ratio of the actual heat gain delivered by the collector (equation 4) to the ideal solar radiation that will be received at the receiver tube when the optical efficiency of the collector was 100% for a concentration ratio of 25. The solar concentrator thermal efficiency was found to be increasing with the proportion of NPs increasing in the base fluid, Therminol®55, as shown in fig. 13. A maximum efficiency of 62.7% was calculated for 0.1 vol% Al_2O_3 nHTF. It was found that the sun-tracker employed was faulty and it could align the lens aperture normal to the direction of incident solar radiation, a deviation of up to 20° was measured. Hence, the solar tracker was disabled and the lens and receiver tube assembly was manually inclined for normal incidence at the beginning of every half-hour intervals and held at that this fixed tilt angle through the half an hour. This arrangement decreased the optical performance of the solar collector which is evident from the highest temperature achieved by the working fluid in the tank. However, the experiment has successfully demonstrated the advantage of using nHTFs to directly absorb solar radiation in visible spectrum. Addition of nanoparticles clearly enhance the optical and thermal performance of the nHTF by enhancing refractive index and absorptivity. Much higher tank temperatures and corresponding higher solar to thermal conversion efficiencies can be achieved with optical efficiencies of >90%.

4. Conclusions

Thermal and optical properties of nHTF comprising Al_2O_3- Therminol®55 with a range of volumetric proportions of Al_2O_3 (0.025 vol% - 0.3 vol%) have been experimentally evaluated and characterised for their use as directly solar absorbing working fluid in line-axis (Fresnel lens based) solar concentrator for supplying heat. The main conclusions of the study summarised as follows:

(i) The zeta potential values of >36 recorded for nHTFs containing up to 0.1 vol% concentration of Al_2O_3 revealed that suspensions are sufficiently stable for use in solar thermal collectors. However, nHTFs with higher concentrations, 0.2 vol% and 0.3 vol% were found to have less zeta potential value of <25, which means lower stability due to risk of sedimentation of NPs; these higher concentration nHTFs are therefore concluded to be unfit for their use in the solar collector applications where fluid might not be circulating in the hours of low or nil sunshine.

(ii) The addition of NPs was found to increase the thermal conductivity of nHTF rapidly at low concentrations (≤0.1 vol%) and gradually at higher concentrations. Highest enhancement in thermal conductivity of 11.7% was measured for 0.1 vol% Al_2O_3 concentration nHTF. However, a further increase in concentration reduced thermal conductivity due to unstablility caused by potential agglomeration and sedimentation.

(iii) Refractive index of nHTFs followed a trend similar to that of thermal conductivity whereby a rise was measured up to a Al_2O_3 concentration of 0.1 vol% and fall beyond this concentration level due to potential increase in agglomeration of NPs.

(iv) Absorbance of the nHTF increased with an increase in the concentration of Al_2O_3 NPs due to direct absorption of electromagnetic radiation by the nanoparticles. The point of maximum absorbance occurred at a higher wavelength as the NP concentration was increased.

(v) Due to favourable thermal conductivity, refractive index and absorptivity of nHTFs measured a highest temperature of 132.8 °C was delivered by the solar collector at 13:00 pm using 0.1 vol% concentration Al_2O_3 nHTF at a flow rate of 0.5 lps. This is 44.7 °C higher than that achieved by pure Therminol®55 (88.1 °C) even though the DNI during 0.1vol% nHTF test was considerably lower than that for the later.

(vi) The solar concentrator thermal efficiency increased with the proportion of NPs attaining a maximum of 62.7% for 0.1 vol% Al_2O_3 nHTF.

(vii) Directly absorbing nHTFs along with the solar collector developed in this study are predicted to be strong candidates for replacing the conventional metallic tube receiver concentrators due to advantages of size compaction and higher thermal conversion efficiency.

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M. Muraleedharan[1], H. Singh[2*], S. Suresh[1], M. Udayakumar[1]

[1]Department of Mechanical Engineering, National Institute of Technology, Tiruchirappalli, 620015, India
[2] Institute of Energy Futures, Brunel University London, Kingston Lane, Uxbridge, UB8 3PH, UK

[*] Corresponding author Email: harjit.singh@brunel.ac.uk; Tel: +44-(0)20-87514442

Abstract

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Keywords: Therminol-55, Alumina (Al_2O_3) nanoparticles, Nano heat transfer fluid, Thermal conductivity, Zeta potential, specific heat, refractive index, Concentrating solar collector, Linear Fresnel lens.

1. Introduction

Thermal, flow and optical properties of nHTFs are of particular interest due to their potential use as directly absorbing working fluid in solar collectors. Dispersion of nanoparticles (NPs) in conventional heat transfer fluids has been shown to improve their thermal properties, for example, references [1-3]. Chandrasekar et al. [2] experimentally measured thermal conductivity of Al_2O_3-water nHTF, for NP concentration varying from 0.33 vol% to 5 vol%, to be higher than that of water. Sani et al. [4] reported optical characterisation of nHTF comprising single-wall carbon nano horns and ethylene glycol. Hordy et al. [5] studied stability of plasma functionalized multi-walled carbon nanotubes suspension in ethylene glycol and propylene glycol at 170 °C for 8 months. Agglomeration was found to occur in non-polar Therminol VP-1 heat transfer fluid. Gupta et al. [6] reported a 39.6% rise in instantaneous efficiency for a flat plate solar collector when directly absorbing Al_2O_3-water nHTF nanofluid with 20 nm Al_2O_3 nanoparticles 0.005 vol% was used. A clear optimum volume faction of 0.005% was observed due to a concomitant increase in heat loss as the solar absorption increased. Taylor et al. [7] described modelling and experimental methods to determine the optical properties of nHTFs. Khullar et al. [8] theoretically predicted a 5–10% higher efficiency for a parabolic concentrator using nHTF consisting of spherical aluminium NPs suspended in Therminol VP-1 than a conventional parabolic solar collector. Anoop et al. [9] reported a rise in refractive index by <1% with an increase in nanoparticle loadings in SiO_2 - water nHTF. Said et al. [10, 11] investigated the effect of size and concentration of TiO_2 NPs on optical properties of nHTF. The size of NPs (TiO_2 and Al_2O_3) was found to have a nominal effect on optical properties of water based nHTFs while the extinction coefficient increased linearly with increase in volumetric concentration. Also, it was found that TiO_2 had better optical properties than Al_2O_3, but it formed a less stable suspension in water than the later. Thermo-physical characterisation of Therminol®55 based nHTFs containing MgO NPs [12] and CuO NPs [13] have also been reported.

This paper reports the results of an experimental investigations ino the suitability of Al_2O_3- Therminol® 55 based nHTF as directly absorbing working fluid for solar thermal concentrating collectors. Therminol®55 was preferred because of its stable physical and thermal properties over the temperature ~~rage~~ range of interest, ≤200°C [12], and Al_2O_3 for superior thermal and optical properties [3]. To the best of authors' knowledge, this is the first study reporting experimentally measured thermal, physical and optical characteristics of Al_2O_3-Therminol®55 nHTF and its real life performance as directly absorbing working fluid in a line axis solar concentrating collector comprising linear Fresnel lens.

2. Experimental details

2.1 nHTF preparation

Fig.1 shows the methodology adopted for the preparation of alumina (Al_2O_3)-Therminol®55 nHTF and its characterization. Commercially available spherical Al_2O_3 [14] nanoparticles with 99.5% purity (refractive index of 1.768 and surface area 32-40 m^2/g) were used to prepare nHTF. Surface morphology and microstructure of the nano particles was observed using a scanning electron microscope. SEM images of alumina at ~~200,00x~~ X20,000 and ~~30,00x~~ X30,000 are shown in Fig. 2. Images showed the spherical shape of alumina nanoparticles with an average size of 30 to 40 nm.

Therminol-55 [15] was used as the base fluid and Oleic acid [16] as surfactant because of its good miscibility and comparative viscosity with Therminol®55. The amount of nanoparticles added to the base fluid to achieve a particular volumetric concentration (ϕ) was calculated using equation (1).

$$\phi = \frac{W_{np}/\rho_{np}}{W_{np}/\rho_{np}+W_{bf}/\rho_{bf}} \quad (1)$$

Where

W_{np} is the mass of NPs

ρ_{np} is the density of NPs

W_{bf} is the mass of base fluid

ρ_{bf} is density of base fluid

Mixture containing 0.5 mL of oleic acid per gram of Al_2O_3 NPs was first prepared [11] and dispersed into Therminol®55 using a magnetic stirrer for 45 minutes. Further to improve the stability of the nHTF sonication was done using an ultrasonic bath for 45 minutes. This procedure was followed to prepare samples of nHTF containing different volumetric concentrations of Al_2O_3, 0.025 vol%, 0.05 vol%, 0.075 vol%, 0.1 vol%, 0.2 vol% and 0.3 vol%. Fig. 3 shows samples of the nHTFs prepared with the fluid colour getting

paler as the concentration of NPs increased. Table 1 details the amount of Al_2O_3 and oleic acid used to prepare the nHTFs employed in the study.

2.2 Characterization of Al_2O_3–Therminol®55 nHTF

Stability of the nHTF samples was determined through measuring Zeta potential of nHTFs. Zeta potential is the physical property exhibited by any particle in suspension and is the electrostatic attraction or repulsion between the surface of the solid particle immersed in a conducting liquid and the bulk of the liquid. Zetasizer Nano ZS equipment [17], ~~shown in Fig. 4a,~~ was used to measure zeta potential. It is a high performance two angle particle and molecular size analyser for enhanced detection of aggregates and measurement of small or dilute samples and samples at very high or low concentration. Large zeta potentials either positive or negative indicate more stable dispersion. The thermal conductivity of the samples was measured using KD2 Pro Thermal Properties Analyser [18] ~~shown in Fig. 4b~~. The absorbance of the nHTF was measured using UV-Vis spectrophotometer [19]~~, Fig. 4c,~~ for 400nm to 900nm wavelength at 25°C. ~~It is a double beam spectrophotometer in which one beam passes through the sample and the other through the reference sample, and it quantitatively compares the amount of light passing through the test and reference sample~~. It is a double beam spectrophotometer in which one beam passes through the sample and the other through the reference sample, and it quantitatively compares the spectral transmission of light passing through the test and reference sample.

~~Refractive index, an important parameter pertaining the nHTFs used as directly absorbing working fluids, such as those developed in this study, was measured using a Rudolph Research - J257 refract metre [18], Fig. 4d, for a wavelength of 589.3nm at 25°C.~~

Propagation of light through a medium depends on its refractive index, which is a measure of the time taken by visible solar radiation to pass through a layer of fluid. Higher is the refractive index of fluid longer would be the time taken by radiation to traverse through it, which in turn enhances the absoption of light in the fluid layer [20]. Therefore, refractive index, an important parameter pertaining the nHTFs used as directly absorbing working fluids, such as those developed in this study, was measured using a Rudolph Research - J257 refractometer [21], for a wavelength of 589.3nm at 25°C. Water with a refractive index of

1.333 was taken as a reference sample. Specifications of the equipment used for characterization ~~instruments~~ are detailed in Table 2.

2.3 Performance of nHTF in line-axis solar concentrator

The directly absorbing nHTFs was tested under real life outdoor conditions using a concentrating solar collector system specifically developed for this purpose during the study. The concentrator comprised four flat line-axis Fresnel lenses focusing visible solar radiation at four evacuated glass receiver tubes, a single-axis tracking system and a storage tank as shown in ~~Fig. 5~~.Fig. 4. Lens and receiver tube details are provided in Table 3. The collector was held in true North-South direction (surface azimuth angle 0°) and tracked about this axis to follow the movement of sun along East-West axis.

The receiver tubes consisted of an outer glass tube (external diameter 25 mm) surrounding an inner glass tube (internal diameter 10mm). The annular space between the outer and inner tubes was evacuated to a low air pressure of 10^{-3} mbar to suppress the convective heat loss from the warmer nHTF flowing through the internal tube to the surroundings. The four receiver tubes were located parallel to each other with each positioned directly below a Fresnel lens in such a way that the central long axis of a tube fell exactly on the focal line of the corresponding Fresnel lens just above it. The solar concentrator developed during the study is shown in ~~Fig.6~~Fig. 5 with ~~Fig. 6a~~Fig. 5a showing the concentrator being tested outdoors and ~~Fig. 6b~~Fig. 5b an illuminated receiver tube containing nHTF. Receiver tubes were connected in series such as the nHTF flows from one tube to another through an insulated flexible hose, see ~~Fig. 6~~Fig. 4 and ~~Fig 6(a)~~ Fig 5(a). Global and diffused radiation were measured using pyranometers, one located in the shade and other directly on the inlet aperture plane of Fresnel lenses.

The Fresnel lens and receiver tubes were supported by an aluminium box frame and the Fresnel lenses and the receiver tubes assembly were tracked by a single axis tracking system. During testing the directly absorbing nHTF was pumped into the Fresnel lens concentrator at a constant flow rate of 0.5 lps using a rotameter and two control valves as shown in ~~Fig. 5.~~Fig. 4. Four calibrated k-type thermocouples (accuracy ±0.5 C) were deployed at the outlet of each receiver to measure nHTF temperatures.

3. Results and Discussions

3.1 Stability analysis by zeta potential test

Quantitative stability of Al_2O_3-Therminol®55 nHTFs prepared during the study was determined using zeta potential test. All the characteristic studies were carried out one week after the sample preparation. The sample with 0.025 vol% Al_2O_3 returned the highest zeta potential value of 52.4 mV; the zeta potential values reduced with an increase in Al_2O_3 concentration. ~~Fig.7~~Fig. 6 shows the zeta potential distribution curve of 0.1 vol% concentration with Table 4 detailing the zeta potential values measured for the full range of the nHTFs studied.

It can be seen in Table 4 that an increase in the volumetric concentration of Al_2O_3 decrased zeta potential from 52.4 for 0.025 vol% to 24.8 for 0.3 vol%. A moderate fall in the stability of nHTF from 0.025 vol% till 0.1 vol% and a significant fall for concentrations >0.1 vol% can be seen. This behaviour can be attributed to the potential NPs agglomeration leading to settling down of Al_2O_3 in the solution as the NP concenration increases.

3.2 Thermal conductivity

The addition of nanoparticles enhanced the thermal conductivity of Therminol®55 nHTF even at a low loading of 0.025 vol% concentration of $Al_2O_{3.}$ Measured thermal conductivity values for the nHTFs over a full range of volumetric concentrations of Al_2O_3 in Therminol®55 are shown in ~~Fig. 8.~~Fig. 7. A clear maxima in thermal conductivity values was observed for nHTF with 0.1 vol% Al_2O_3. It achieved a maximum enhancement of 11.7% with an Al_2O_3 concentration of 0.1 vol%. Improvement in thermal conductivity was attributed to Brownian motion, nanoparticles clustering and liquid layering at liquid-nanoparticle interface. A drop in the thermal conductivity values was observed for Al_2O_3 concentrations of 0.2 vol% and 0.3 vol%, which is attributed to increased agglomeration at these concentrations. The increased agglomeration at higher concentrations was also indicated by lower zeta potential values, see Table 4.

3.3 Refractive index

Refractive indices for the nHTFs were measured at the optical wavelength of 589.3 nm at 25°C, see ~~Fig. 8.~~Fig. 7. The refractive index of alumina NPs employed is 1.768. The refractive index of Therminol®55 was measured to be 1.4858 and that of the nHTF with 0.025 vol % Al_2O_3 1.48607, indicating a rapid rise due to the presence of NPs. A further increase in the concentration of NPs increased the refractive index, though gradually, up to an Al_2O_3 concentration of 0.1 vol% beyond which (for 0.2 vol% and 0.3 vol% concentrations) refractive index decreased, a trend attributed to increased agglomeration of NPs.

3.4 Absorbance

~~Fig.9~~ Fig. 8 shows the measured absorbance spectra of the Al_2O_3-Therminol®55 nHTFs over the wavelength range of 400-900 nm at 25° C. Absorbance increased with an increase in the concentration of Al_2O_3 NPs due to direct absorption of electromagnetic radiation by the nanoparticles. Increase in the Al_2O_3 concentration resulted into a clear increase in the absorbance values. Also the point of maximum absorbance shifted towards right (to a higher wavelength) as the volumetric concentration of Al_2O_3 was increased, see ~~Fig. 9.~~Fig. 8. The maximum absorbance for nHTF with 0.025 vol% was measured at 410nm, for 0.05 vol% at 444nm, for 0.075 vol% at 459nm and for 0.1 vol% at 501nm.

3.5 Testing of directly absorbing nHTF as working fluid in line-focussing solar concentrating collector

The developed solar collector, shown in ~~Fig. 6a~~ Fig. 5a was tested outdoor under real life ambient and solar conditions at National Institute of Technology, Tiruchirappalli (India), using nHTFs synthesised containing Al_2O_3 in the concentrations of 0.025 vol%, 0.05 vol%, 0.075 vol% and 0.1 vol%. Decision to use nHTFs with Al_2O_3 concentration of ≤0.1 vol% was based on thermal conductivity, suspension stability and optical measurements described in the previous sections. During each test nHTF temperature at the outlet of each receiver tube and solar radiation intensity (global and diffuse) were measured. Tests were performed on comparatively sunnier days during the months of April to June 2016. The flow rate of the working fluid during all experiments was maintained at 0.5 lpm and measured using a rotameter. Experimental data was acquired using a data logger, Keysight 34972.

3.5.1 Direct normal incidence (DNI) radiation at the inlet apertur of the concentrator

One pyranometer was employed to measure the tilted (on Fresnel lens inlet aperture plane) global radiation and other for horizontal diffuse solar radiation during the full duration of the project. Using the measured global and diffuse radiation, DNI incident at the tilted inlet aperture of the solar collector was calculated employing the Maxwell Direct Insolation Simulation Code model ~~[21]~~[22]. The resulting DNI for the specific hours of testing is shown in ~~Fig.10.~~Fig. 9. Instead of giving the specific dates for which this data was calculated for, we have specified the nHTF to which any DNI curve corresponds. This is done to enable the reader to easily relate the data among various figures. It's clear from ~~fig. 10~~ Fig. 9 that among all the test days, the least sunny was the one on which the tests were run for nHTF containing 0.1% concentration of Al_2O_3. The other days were more or less similarly sunny.

3.5.2 Thermal performance of the solar collector system

The instantaneous temperatures at the outlets of the solar collector receiver tubes recorded at half hourly intervals are shown in ~~Fig. 11.~~Fig. 10. These were recorded at the outlet of the fourth receiver tube from where the nHTF flows into the storage tank. Temperature of nHTF increased with a rise in Al_2O_3 NP concentration even though the solar DNI intensity at any half hourly interval remained nearly the same during testing, see ~~Fig.10.~~Fig. 9. It is concluded that the presence of Al_2O_3 NPs increased the solar radiation absorption due to high ~~absorptivity and refractive index~~ refractive index and absorptivity, see ~~Fig. 8~~Fig. 7 and ~~Fig. 9~~Fig. 8, and also that the absorbed radiation was converted into thermal energy, which was responsible for the temperature rise in nHTF. The highest temperature of 132.8 °C was achieved at 13:00 pm by the 0.1 vol% nHTF, 44.7 °C higher than that achieved by pure Therminol®55 fluid (88.1 °C) even though the DNI during 0.1 vol% nHTF test was lower than that for pure Therminol®55. Temperatures achieved at half hourly intervals for different nHTFs can be seen from ~~Fig.11~~ Fig. 10 with ~~Fig.10~~Fig. 9 showing the DNI incident at the Fresnel lens inlet aperture.

Net energy gain delivered by the solar collector (Q_u) was calculated by using equation (2) employing the storage tank temperatures recorded before and after the experiment for every half hour.

$$Q_u = m_{sto} c_p \left(T_{sto,f} - T_{sto,i}\right) \quad (2)$$

Where

m_{sto} is the mass of nHTF in the storage tank

c_p is the specific heat of nHTF

$T_{sto,i}$ is the temperature of nHTF in the storage tank at the beginning of every half hour interval

$T_{sto,f}$ is the temperature of nHTF in the storage tank after every half hour interval

Thermo-physical properties such as specific heat (c_p) and density (ρ) of nanofluids consisting of various permutations of nanoparticles and Therminol®55 were computed by applying a parallel mixture rule for an effective property (P), shown in equation 3 (Khullar et al., 2012; Chandrasekar et al., 2009).

$$P = f_v P_{np} + (1 - f_v) P_{bf} \tag{3}$$

where

f_v is the volumetric fraction of the nanoparticles in the nHTF

P_{np} is the property of the nanoparticles (Al_2O_3)

P_{bf} is the property of the base fluid (Therminol®55)

Due to a low concentration of nanoparticles (0.025 vol% - 0.1vol%) dispersed in the base fluid, Therminol®55, these marginally affected base fluid properties, such as mass density and specific heat, at any given temperature, see ~~Fig. 12~~ Fig. 11for mass density and table 5 for specific heat.

Thermal loss from the solar collector components such as radiative loss from receiver tubes and radiative and convective heat loss from the storage tank and connecting hose were calculated using the expression (4).

$$\varepsilon \sigma A\left(T^4 - {T_s}^4\right) + hA(T - T_a) \tag{4}$$

where

ε is the radiative emissivity of the solar collector component, storage tank, hose, glass receiver tube or working fluid

σ is the Stefan Boltzmann constant

A is the relevant area of heat transfer of the component

h is the convective heat transfer between the solar collector component and ambient

T is the temperature of the component

T_s is the sky temperature

T_a is the ambient temperature

Radiative emissivity for the collector components was assumed to be constant with temperature. For example, for glass receiver tube the emissivity was assumed to have a constant value of 0.9 (Duffie & Beckman, 2006) and polyethylene hose 0.1. The storage tank (300mm diameter, 400mm high) was insulated with 50mm thick glass wool insulation (thermal conductivity 0.04 W/m.K). Radiative loss from nHTF contained in glass receiver tube was calculated assuming the inner glass tube surface temperature to be equal to that of the nHTF at any instant. No low emissivity coatings were employed in the glass tubes employed for the experiment. Any convective loss from the inner glass tube to the outer was neglected due to a low vacuum pressure maintained in the annulus between inner and outer tube. This was verified by measuring the surface temperature of the outer glass tube which remained within 1°C of the ambient temperature all through the experiments. Any conductive or radiative loss from the tank to ground loss were neglected. Any radiative loss from the insulated polyethylene tube connecting the glass receiver tubes and the tank was neglected.

Convective loss coefficient (h) from connecting hose (total length 3m) and storage tank to surrounding air was calculated using equation 5 (Duffie & Beckman, 2006).

$$Nu = \frac{h.D}{k} = 0.4 + 0.54Re^{0.52} \quad (5)$$

where

Re is the Reynolds number

D is the diameter

k is the thermal conductivity of surrounding air

The solar concentrator thermal efficiency was calculated as the ratio of the actual heat gain delivered by the collector (equation 4) to the ideal solar radiation that will be received at the receiver tube when the optical efficiency of the collector was 100% for a concentration ratio of 25. The solar concentrator thermal efficiency was found to be increasing with the proportion of NPs increasing in the base fluid, Therminol®55, as shown in fig. 13.Fig. 12. A maximum efficiency of 62.7% was calculated for 0.1 vol% Al_2O_3 nHTF. It was found that the sun-tracker employed was faulty and it could align the lens aperture normal to the direction of incident solar radiation, a deviation of up to 20° was measured. Hence, the solar tracker was disabled and the lens and receiver tube assembly was manually inclined for normal incidence at the beginning of every half-hour intervals and held at that this fixed tilt angle through the half an hour. This arrangement decreased the optical performance of the solar collector which is evident from the highest temperature achieved by the working fluid in the tank. However, the experiment has successfully demonstrated the advantage of using nHTFs to directly absorb solar radiation in visible spectrum. Addition of nanoparticles clearly enhance the optical and thermal performance of the nHTF by enhancing refractive index and absorptivity. Much higher tank temperatures and corresponding higher solar to thermal conversion efficiencies can be achieved with optical efficiencies of >90%.

4. Conclusions

Thermal and optical properties of nHTF comprising Al_2O_3- Therminol®55 with a range of volumetric proportions of Al_2O_3 (0.025 vol% - 0.3 vol%) have been experimentally evaluated and characterised for their use as directly solar absorbing working fluid in line-axis (Fresnel lens based) solar concentrator for supplying heat. The main conclusions of the study summarised as follows:

(i) The zeta potential values of >36 recorded for nHTFs containing up to 0.1 vol% concentration of Al_2O_3 revealed that suspensions are sufficiently stable for use in solar thermal collectors. However, nHTFs with higher concentrations, 0.2 vol% and 0.3 vol% were found to have less zeta potential value of <25, which means lower stability due to risk of sedimentation of NPs; these higher concentration nHTFs are therefore concluded to be unfit for their use in the solar collector applications where fluid might not be circulating in the hours of low or nil sunshine.

(ii) The addition of NPs was found to increase the thermal conductivity of nHTF rapidly at low concentrations (≤0.1 vol%) and gradually at higher concentrations. Highest enhancement in thermal conductivity of 11.7% was measured for 0.1 vol% Al_2O_3 concentration nHTF. However, a further increase in concentration reduced thermal conductivity due to unstablility caused by potential agglomeration and sedimentation.

(iii) Refractive index of nHTFs followed a trend similar to that of thermal conductivity whereby a rise was measured up to a Al_2O_3 concentration of 0.1 vol% and fall beyond this concentration level due to potential increase in agglomeration of NPs.

(iv) Absorbance of the nHTF increased with an increase in the concentration of Al_2O_3 NPs due to direct absorption of electromagnetic radiation by the nanoparticles. The point of maximum absorbance occurred at a higher wavelength as the NP concentration was increased.

(v) Due to favourable thermal conductivity, refractive index and absorptivity of nHTFs measured a highest temperature of 132.8 °C was delivered by the solar collector at 13:00 pm using 0.1 vol% concentration Al_2O_3 nHTF at a flow rate of 0.5 lps. This is 44.7 °C higher than that achieved by pure Therminol®55 (88.1 °C) even though the DNI during 0.1vol% nHTF test was considerably lower than that for the later.

(vi) The solar concentrator thermal efficiency increased with the proportion of NPs attaining a maximum of 62.7% for 0.1 vol% Al_2O_3 nHTF.

(vii) Directly absorbing nHTFs along with the solar collector developed in this study are predicted to be strong candidates for replacing the conventional metallic tube receiver concentrators due to advantages of size compaction and higher thermal conversion efficiency.

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Directly absorbing Therminol-Al_2O_3 nano heat transfer fluid for linear solar concentrating collectors

M. Muraleedharan[1], H. Singh[2*], S. Suresh[1], M. Udayakumar[1]

[1]Department of Mechanical Engineering, National Institute of Technology, Tiruchirappalli, 620015, India

[2] Institute of Energy Futures, Brunel University London, Kingston Lane, Uxbridge, UB8 3PH, UK

[*] Corresponding author Email: harjit.singh@brunel.ac.uk; Tel: +44-(0)20-87514442

Abstract

This paper reports experimentally measured thermal and optical properties of Al_2O_3 - Therminol®55 nano heat transfer fluid (nHTF) in conjunction with a specially developed line focussing Fresnel lens based solar thermal concentrator. Solar collector tests were conducted under real life outdoor ambient and solar radiation conditions. A range of volumetric proportions of Al_2O_3 (0.025 vol% - 0.3 vol%) have been covered. Highest thermal conductivity and refractive index were measured for nHTF with 0.1 vol% concentration of Al_2O_3 with higher concentrations (>0.1 vol%) concluded to be unfit for their use in the solar collector applications due to likely agglomeration and sedimentation in the hours of low or nil sunshine when fluid is not circulating. Thermal conductivity enhanced by 11.7% for 0.1 vol% Al_2O_3 concentration nHTF. A highest temperature of 132.8 °C was delivered by the solar collector using 0.1% concentration Al_2O_3 nHTF at a flow rate of 0.5lps. This was 44.7 °C higher than that achieved by pure Therminol®55 (88.1 °C) even though the DNI during 0.1% nHTF test was considerably lower than that for the later. The solar concentrator thermal efficiency increased with the proportion of NPs attaining a maximum of 52.2% for 0.1vol% Al_2O_3 nHTF. Directly absorbing nHTFs along with the solar collector developed in this study are predicted to be strong candidate to replace conventional metallic tube receiver using concentrators due to advantages of size compaction and higher thermal conversion efficiency.

Keywords: Therminol-55, Alumina (Al_2O_3) nanoparticles, Nano heat transfer fluid, Thermal conductivity, Zeta potential, specific heat, refractive index, Concentrating solar collector, Linear Fresnel lens.

1. Introduction

Thermal, flow and optical properties of nHTFs are of particular interest due to their potential use as directly absorbing working fluid in solar collectors. Dispersion of nanoparticles (NPs) in conventional heat transfer fluids has been shown to improve their thermal properties, for example, references [1-3]. Chandrasekar et al. [2] experimentally measured thermal conductivity of Al_2O_3-water nHTF, for NP concentration varying from 0.33 vol% to 5 vol%, to be higher than that of water. Sani et al. [4] reported optical characterisation of nHTF comprising single-wall carbon nano horns and ethylene glycol. Hordy et al. [5] studied stability of plasma functionalized multi-walled carbon nanotubes suspension in ethylene glycol and propylene glycol at 170 °C for 8 months. Agglomeration was found to occur in non-polar Therminol VP-1 heat transfer fluid. Gupta et al. [6] reported a 39.6% rise in instantaneous efficiency for a flat plate solar collector when directly absorbing Al_2O_3-water nHTF nanofluid with 20 nm Al_2O_3 nanoparticles 0.005 vol% was used. A clear optimum volume faction of 0.005% was observed due to a concomitant increase in heat loss as the solar absorption increased. Taylor et al. [7] described modelling and experimental methods to determine the optical properties of nHTFs. Khullar et al. [8] theoretically predicted a 5–10% higher efficiency for a parabolic concentrator using nHTF consisting of spherical aluminium NPs suspended in Therminol VP-1 than a conventional parabolic solar collector. Anoop et al. [9] reported a rise in refractive index by <1% with an increase in nanoparticle loadings in SiO_2 - water nHTF. Said et al. [10, 11] investigated the effect of size and concentration of TiO_2 NPs on optical properties of nHTF. The size of NPs (TiO_2 and Al_2O_3) was found to have a nominal effect on optical properties of water based nHTFs while the extinction coefficient increased linearly with increase in volumetric concentration. Also, it was found that TiO_2 had better optical properties than Al_2O_3, but it formed a less stable suspension in water than the later. Thermo-physical characterisation of Therminol®55 based nHTFs containing MgO NPs [12] and CuO NPs [13] have also been reported.

This paper reports the results of an experimental investigations ino the suitability of Al_2O_3- Therminol® 55 based nHTF as directly absorbing working fluid for solar thermal concentrating collectors. Therminol®55 was preferred because of its stable physical and thermal properties over the temperature range of interest, ≤200°C [12], and Al_2O_3 for superior thermal and optical properties [3]. To the best of authors' knowledge, this is the first study reporting experimentally measured thermal, physical and optical characteristics of Al_2O_3-Therminol®55 nHTF and its real life performance as directly absorbing working fluid in a line axis solar concentrating collector comprising linear Fresnel lens.

2. Experimental details

2.1 nHTF preparation

Fig.1 shows the methodology adopted for the preparation of alumina (Al_2O_3)-Therminol®55 nHTF and its characterization. Commercially available spherical Al_2O_3 [14] nanoparticles with 99.5% purity (refractive index of 1.768 and surface area 32-40 m^2/g) were used to prepare nHTF. Surface morphology and microstructure of the nano particles was observed using a scanning electron microscope. SEM images of alumina at X20,000 and X30,000 are shown in Fig. 2. Images showed the spherical shape of alumina nanoparticles with an average size of 30 to 40 nm.

Therminol-55 [15] was used as the base fluid and Oleic acid [16] as surfactant because of its good miscibility and comparative viscosity with Therminol®55. The amount of nanoparticles added to the base fluid to achieve a particular volumetric concentration (ϕ) was calculated using equation (1).

$$\phi = \frac{W_{np}/\rho_{np}}{W_{np}/\rho_{np} + W_{bf}/\rho_{bf}} \quad (1)$$

Where

W_{np} is the mass of NPs

ρ_{np} is the density of NPs

W_{bf} is the mass of base fluid

ρ_{bf} is density of base fluid

Mixture containing 0.5 mL of oleic acid per gram of Al_2O_3 NPs was first prepared [11] and dispersed into Therminol®55 using a magnetic stirrer for 45 minutes. Further to improve the stability of the nHTF sonication was done using an ultrasonic bath for 45 minutes. This procedure was followed to prepare samples of nHTF containing different volumetric concentrations of Al_2O_3, 0.025 vol%, 0.05 vol%, 0.075 vol%, 0.1 vol%, 0.2 vol% and 0.3 vol%. Fig. 3 shows samples of the nHTFs prepared with the fluid colour getting

paler as the concentration of NPs increased. Table 1 details the amount of Al_2O_3 and oleic acid used to prepare the nHTFs employed in the study.

2.2 Characterization of Al_2O_3–Therminol®55 nHTF

Stability of the nHTF samples was determined through measuring Zeta potential of nHTFs. Zeta potential is the physical property exhibited by any particle in suspension and is the electrostatic attraction or repulsion between the surface of the solid particle immersed in a conducting liquid and the bulk of the liquid. Zetasizer Nano ZS equipment [17], was used to measure zeta potential. It is a high performance two angle particle and molecular size analyser for enhanced detection of aggregates and measurement of small or dilute samples and samples at very high or low concentration. Large zeta potentials either positive or negative indicate more stable dispersion. The thermal conductivity of the samples was measured using KD2 Pro Thermal Properties Analyser [18]. The absorbance of the nHTF was measured using UV-Vis spectrophotometer [19]-for 400nm to 900nm wavelength at 25°C. It is a double beam spectrophotometer in which one beam passes through the sample and the other through the reference sample, and it quantitatively compares the spectral transmission of light passing through the test and reference sample.

Propagation of light through a medium depends on its refractive index, which is a measure of the time taken by visible solar radiation to pass through a layer of fluid. Higher is the refractive index of fluid longer would be the time taken by radiation to traverse through it, which in turn enhances the absoption of light in the fluid layer [20]. Therefore, refractive index, an important parameter pertaining the nHTFs used as directly absorbing working fluids, such as those developed in this study, was measured using a Rudolph Research - J257 refractometer [21], for a wavelength of 589.3nm at 25°C. Water with a refractive index of 1.333 was taken as a reference sample. Specifications of the equipment used for characterization are detailed in Table 2.

2.3 Performance of nHTF in line-axis solar concentrator

The directly absorbing nHTFs was tested under real life outdoor conditions using a concentrating solar collector system specifically developed for this purpose during the study.

The concentrator comprised four flat line-axis Fresnel lenses focusing visible solar radiation at four evacuated glass receiver tubes, a single-axis tracking system and a storage tank as shown in Fig. 4. Lens and receiver tube details are provided in Table 3. The collector was held in true North-South direction (surface azimuth angle 0°) and tracked about this axis to follow the movement of sun along East-West axis.

The receiver tubes consisted of an outer glass tube (external diameter 25 mm) surrounding an inner glass tube (internal diameter 10mm). The annular space between the outer and inner tubes was evacuated to a low air pressure of 10^{-3} mbar to suppress the convective heat loss from the warmer nHTF flowing through the internal tube to the surroundings. The four receiver tubes were located parallel to each other with each positioned directly below a Fresnel lens in such a way that the central long axis of a tube fell exactly on the focal line of the corresponding Fresnel lens just above it. The solar concentrator developed during the study is shown in Fig. 5 with Fig. 5a showing the concentrator being tested outdoors and Fig. 5b an illuminated receiver tube containing nHTF. Receiver tubes were connected in series such as the nHTF flows from one tube to another through an insulated flexible hose, see Fig. 4 and Fig 5(a). Global and diffused radiation were measured using pyranometers, one located in the shade and other directly on the inlet aperture plane of Fresnel lenses.

The Fresnel lens and receiver tubes were supported by an aluminium box frame and the Fresnel lenses and the receiver tubes assembly were tracked by a single axis tracking system. During testing the directly absorbing nHTF was pumped into the Fresnel lens concentrator at a constant flow rate of 0.5 lps using a rotameter and two control valves as shown in Fig. 4. Four calibrated k-type thermocouples (accuracy ±0.5 C) were deployed at the outlet of each receiver to measure nHTF temperatures.

3. Results and Discussions

3.1 Stability analysis by zeta potential test

Quantitative stability of Al_2O_3-Therminol®55 nHTFs prepared during the study was determined using zeta potential test. All the characteristic studies were carried out one week after the sample preparation. The sample with 0.025 vol% Al_2O_3 returned the highest zeta potential value of 52.4 mV; the zeta potential values reduced with an increase in Al_2O_3 concentration. Fig. 6 shows the zeta potential distribution curve of 0.1 vol% concentration with Table 4 detailing the zeta potential values measured for the full range of the nHTFs studied.

It can be seen in Table 4 that an increase in the volumetric concentration of Al_2O_3 decrased zeta potential from 52.4 for 0.025 vol% to 24.8 for 0.3 vol%. A moderate fall in the stability of nHTF from 0.025 vol% till 0.1 vol% and a significant fall for concentrations >0.1 vol% can be seen. This behaviour can be attributed to the potential NPs agglomeration leading to settling down of Al_2O_3 in the solution as the NP concenration increases.

3.2 Thermal conductivity

The addition of nanoparticles enhanced the thermal conductivity of Therminol®55 nHTF even at a low loading of 0.025 vol% concentration of Al_2O_3. Measured thermal conductivity values for the nHTFs over a full range of volumetric concentrations of Al_2O_3 in Therminol®55 are shown in Fig. 7. A clear maxima in thermal conductivity values was observed for nHTF with 0.1 vol% Al_2O_3. It achieved a maximum enhancement of 11.7% with an Al_2O_3 concentration of 0.1 vol%. Improvement in thermal conductivity was attributed to Brownian motion, nanoparticles clustering and liquid layering at liquid-nanoparticle interface. A drop in the thermal conductivity values was observed for Al_2O_3 concentrations of 0.2 vol% and 0.3 vol%, which is attributed to increased agglomeration at these concentrations. The increased agglomeration at higher concentrations was also indicated by lower zeta potential values, see Table 4.

3.3 Refractive index

Refractive indices for the nHTFs were measured at the optical wavelength of 589.3 nm at 25°C, see Fig. 7. The refractive index of alumina NPs employed is 1.768. The refractive index of Therminol®55 was measured to be 1.4858 and that of the nHTF with 0.025 vol % Al_2O_3 1.48607, indicating a rapid rise due to the presence of NPs. A further increase in the concentration of NPs increased the refractive index, though gradually, up to an Al_2O_3 concentration of 0.1 vol% beyond which (for 0.2 vol% and 0.3 vol% concentrations) refractive index decreased, a trend attributed to increased agglomeration of NPs.

3.4 Absorbance

Fig. 8 shows the measured absorbance spectra of the Al_2O_3-Therminol®55 nHTFs over the wavelength range of 400-900 nm at 25° C. Absorbance increased with an increase in the concentration of Al_2O_3 NPs due to direct absorption of electromagnetic radiation by the nanoparticles. Increase in the Al_2O_3 concentration resulted into a clear increase in the absorbance values. Also the point of maximum absorbance shifted towards right (to a higher wavelength) as the volumetric concentration of Al_2O_3 was increased, see Fig. 8. The maximum absorbance for nHTF with 0.025 vol% was measured at 410nm, for 0.05 vol% at 444nm, for 0.075 vol% at 459nm and for 0.1 vol% at 501nm.

3.5 Testing of directly absorbing nHTF as working fluid in line-focussing solar concentrating collector

The developed solar collector, shown in Fig. 5a was tested outdoor under real life ambient and solar conditions at National Institute of Technology, Tiruchirappalli (India), using nHTFs synthesised containing Al_2O_3 in the concentrations of 0.025 vol%, 0.05 vol%, 0.075 vol% and 0.1 vol%. Decision to use nHTFs with Al_2O_3 concentration of $\leq$0.1 vol% was based on thermal conductivity, suspension stability and optical measurements described in the previous sections. During each test nHTF temperature at the outlet of each receiver tube and solar radiation intensity (global and diffuse) were measured. Tests were performed on comparatively sunnier days during the months of April to June 2016. The flow rate of the working fluid during all experiments was maintained at 0.5 lpm and measured using a rotameter. Experimental data was acquired using a data logger, Keysight 34972.

3.5.1 Direct normal incidence (DNI) radiation at the inlet apertur of the concentrator

One pyranometer was employed to measure the tilted (on Fresnel lens inlet aperture plane) global radiation and other for horizontal diffuse solar radiation during the full duration of the project. Using the measured global and diffuse radiation, DNI incident at the tilted inlet aperture of the solar collector was calculated employing the Maxwell Direct Insolation Simulation Code model [22]. The resulting DNI for the specific hours of testing is shown in Fig. 9. Instead of giving the specific dates for which this data was calculated for, we have specified the nHTF to which any DNI curve corresponds. This is done to enable the reader to easily relate the data among various figures. It's clear from Fig. 9 that among all the test days, the least sunny was the one on which the tests were run for nHTF containing 0.1% concentration of Al_2O_3. The other days were more or less similarly sunny.

3.5.2 Thermal performance of the solar collector system

The instantaneous temperatures at the outlets of the solar collector receiver tubes recorded at half hourly intervals are shown in Fig. 10. These were recorded at the outlet of the fourth receiver tube from where the nHTF flows into the storage tank. Temperature of nHTF increased with a rise in Al_2O_3 NP concentration even though the solar DNI intensity at any half hourly interval remained nearly the same during testing, see Fig. 9. It is concluded that the presence of Al_2O_3 NPs increased the solar radiation absorption due to high refractive index and absorptivity, see Fig. 7 and Fig. 8, and also that the absorbed radiation was converted into thermal energy, which was responsible for the temperature rise in nHTF. The highest temperature of 132.8 °C was achieved at 13:00 pm by the 0.1 vol% nHTF, 44.7 °C higher than that achieved by pure Therminol®55 fluid (88.1 °C) even though the DNI during 0.1 vol% nHTF test was lower than that for pure Therminol®55. Temperatures achieved at half hourly intervals for different nHTFs can be seen from Fig. 10 with Fig. 9 showing the DNI incident at the Fresnel lens inlet aperture.

Net energy gain delivered by the solar collector (Q_u) was calculated by using equation (2) employing the storage tank temperatures recorded before and after the experiment for every half hour.

$$Q_u = m_{sto} c_p \left(T_{sto,f} - T_{sto,i}\right) \quad (2)$$

Where

m_{sto} is the mass of nHTF in the storage tank

c_p is the specific heat of nHTF

$T_{sto,i}$ is the temperature of nHTF in the storage tank at the beginning of every half hour interval

$T_{sto,f}$ is the temperature of nHTF in the storage tank after every half hour interval

Thermo-physical properties such as specific heat (c_p) and density (ρ) of nanofluids consisting of various permutations of nanoparticles and Therminol®55 were computed by applying a parallel mixture rule for an effective property (P), shown in equation 3 (Khullar et al., 2012; Chandrasekar et al., 2009).

$$P = f_v P_{np} + (1 - f_v) P_{bf} \tag{3}$$

where

f_v is the volumetric fraction of the nanoparticles in the nHTF

P_{np} is the property of the nanoparticles (Al_2O_3)

P_{bf} is the property of the base fluid (Therminol®55)

Due to a low concentration of nanoparticles (0.025 vol% - 0.1vol%) dispersed in the base fluid, Therminol®55, these marginally affected base fluid properties, such as mass density and specific heat, at any given temperature, see Fig. 11for mass density and table 5 for specific heat.

Thermal loss from the solar collector components such as radiative loss from receiver tubes and radiative and convective heat loss from the storage tank and connecting hose were calculated using the expression (4).

$$\varepsilon \sigma A\left(T^4 - {T_s}^4\right) + hA(T - T_a) \tag{4}$$

where

ε is the radiative emissivity of the solar collector component, storage tank, hose, glass receiver tube or working fluid

σ is the Stefan Boltzmann constant

A is the relevant area of heat transfer of the component

h is the convective heat transfer between the solar collector component and ambient

T is the temperature of the component

T_s is the sky temperature

T_a is the ambient temperature

Radiative emissivity for the collector components was assumed to be constant with temperature. For example, for glass receiver tube the emissivity was assumed to have a constant value of 0.9 (Duffie & Beckman, 2006) and polyethylene hose 0.1. The storage tank (300mm diameter, 400mm high) was insulated with 50mm thick glass wool insulation (thermal conductivity 0.04 W/m.K). Radiative loss from nHTF contained in glass receiver tube was calculated assuming the inner glass tube surface temperature to be equal to that of the nHTF at any instant. No low emissivity coatings were employed in the glass tubes employed for the experiment. Any convective loss from the inner glass tube to the outer was neglected due to a low vacuum pressure maintained in the annulus between inner and outer tube. This was verified by measuring the surface temperature of the outer glass tube which remained within 1°C of the ambient temperature all through the experiments. Any conductive or radiative loss from the tank to ground loss were neglected. Any radiative loss from the insulated polyethylene tube connecting the glass receiver tubes and the tank was neglected.

Convective loss coefficient (h) from connecting hose (total length 3m) and storage tank to surrounding air was calculated using equation 5 (Duffie & Beckman, 2006).

$$Nu = \frac{h.D}{k} = 0.4 + 0.54Re^{0.52} \quad (5)$$

where

Re is the Reynolds number

D is the diameter

k is the thermal conductivity of surrounding air

The solar concentrator thermal efficiency was calculated as the ratio of the actual heat gain delivered by the collector (equation 4) to the ideal solar radiation that will be received at the receiver tube when the optical efficiency of the collector was 100% for a concentration ratio of 25. The solar concentrator thermal efficiency was found to be increasing with the proportion of NPs increasing in the base fluid, Therminol®55, as shown in Fig. 12. A maximum efficiency of 62.7% was calculated for 0.1 vol% Al_2O_3 nHTF. It was found that the sun-tracker employed was faulty and it could align the lens aperture normal to the direction of incident solar radiation, a deviation of up to 20° was measured. Hence, the solar tracker was disabled and the lens and receiver tube assembly was manually inclined for normal incidence at the beginning of every half-hour intervals and held at that this fixed tilt angle through the half an hour. This arrangement decreased the optical performance of the solar collector which is evident from the highest temperature achieved by the working fluid in the tank. However, the experiment has successfully demonstrated the advantage of using nHTFs to directly absorb solar radiation in visible spectrum. Addition of nanoparticles clearly enhance the optical and thermal performance of the nHTF by enhancing refractive index and absorptivity. Much higher tank temperatures and corresponding higher solar to thermal conversion efficiencies can be achieved with optical efficiencies of >90%.

4. Conclusions

Thermal and optical properties of nHTF comprising Al_2O_3- Therminol®55 with a range of volumetric proportions of Al_2O_3 (0.025 vol% - 0.3 vol%) have been experimentally evaluated and characterised for their use as directly solar absorbing working fluid in line-axis (Fresnel lens based) solar concentrator for supplying heat. The main conclusions of the study summarised as follows:

(i) The zeta potential values of >36 recorded for nHTFs containing up to 0.1 vol% concentration of Al_2O_3 revealed that suspensions are sufficiently stable for use in solar thermal collectors. However, nHTFs with higher concentrations, 0.2 vol% and 0.3 vol% were found to have less zeta potential value of <25, which means lower stability due to risk of sedimentation of NPs; these higher concentration nHTFs are therefore concluded to be unfit for their use in the solar collector applications where fluid might not be circulating in the hours of low or nil sunshine.

(ii) The addition of NPs was found to increase the thermal conductivity of nHTF rapidly at low concentrations (≤0.1 vol%) and gradually at higher concentrations. Highest enhancement in thermal conductivity of 11.7% was measured for 0.1 vol% Al_2O_3 concentration nHTF. However, a further increase in concentration reduced thermal conductivity due to unstablility caused by potential agglomeration and sedimentation.

(iii) Refractive index of nHTFs followed a trend similar to that of thermal conductivity whereby a rise was measured up to a Al_2O_3 concentration of 0.1 vol% and fall beyond this concentration level due to potential increase in agglomeration of NPs.

(iv) Absorbance of the nHTF increased with an increase in the concentration of Al_2O_3 NPs due to direct absorption of electromagnetic radiation by the nanoparticles.

The point of maximum absorbance occurred at a higher wavelength as the NP concentration was increased.

(v) Due to favourable thermal conductivity, refractive index and absorptivity of nHTFs measured a highest temperature of 132.8 °C was delivered by the solar collector at 13:00 pm using 0.1 vol% concentration Al_2O_3 nHTF at a flow rate of 0.5 lps. This is 44.7 °C higher than that achieved by pure Therminol®55 (88.1 °C) even though the DNI during 0.1vol% nHTF test was considerably lower than that for the later.

(vi) The solar concentrator thermal efficiency increased with the proportion of NPs attaining a maximum of 62.7% for 0.1 vol% Al_2O_3 nHTF.

(vii) Directly absorbing nHTFs along with the solar collector developed in this study are predicted to be strong candidates for replacing the conventional metallic tube receiver concentrators due to advantages of size compaction and higher thermal conversion efficiency.

Acknowledgement

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30th July 2016

Editor in Chief
Solar Energy journal.

Dear Professor Goswami

We are pleased to be submitting our revised research paper titled "Directly absorbing Therminol –Al_2O_3 nano heat transfer fluid for linear solar concentrating collectors" for publication in the Solar Energy journal.

We thank the reviewers for their valuable time and comments. Our Response to Reviewers document is also attached. We look forward to receiving further comments, if any, from the reviewers whom we thank in anticipation.

Please let me know should you have any queries of your own.

Best regards

Harjit

Harjit Singh
BEng ME PhD

Lecturer in Built Environment Engineering and Energy
Room 131 Howell Building
College of Engineering, Design and Physical Sciences
Brunel University London
Uxbridge, Middlesex UB8 3PH, UK
T +44 (0)1895 265468
E harjit.singh@brunel.ac.uk

Fig. 1

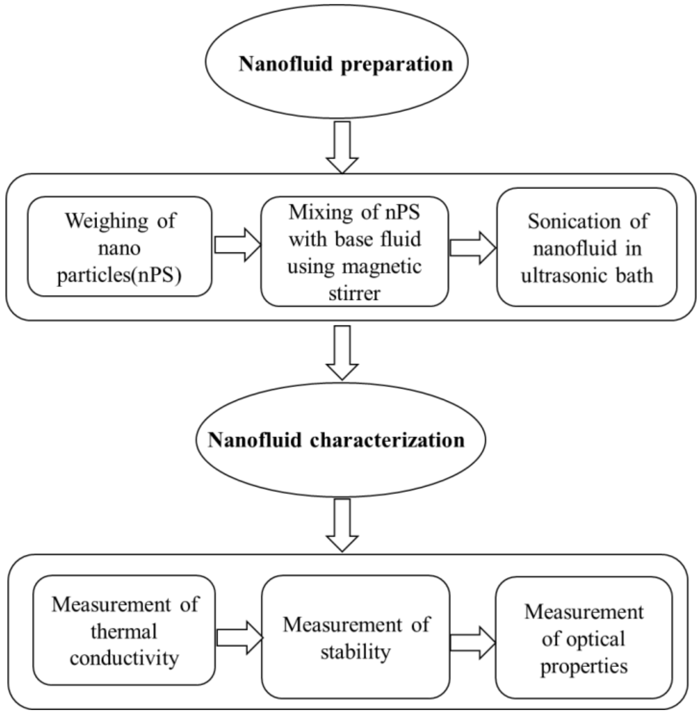


Fig. 1. Procedure for nHTF preparation and characterisation adopted

Fig. 2

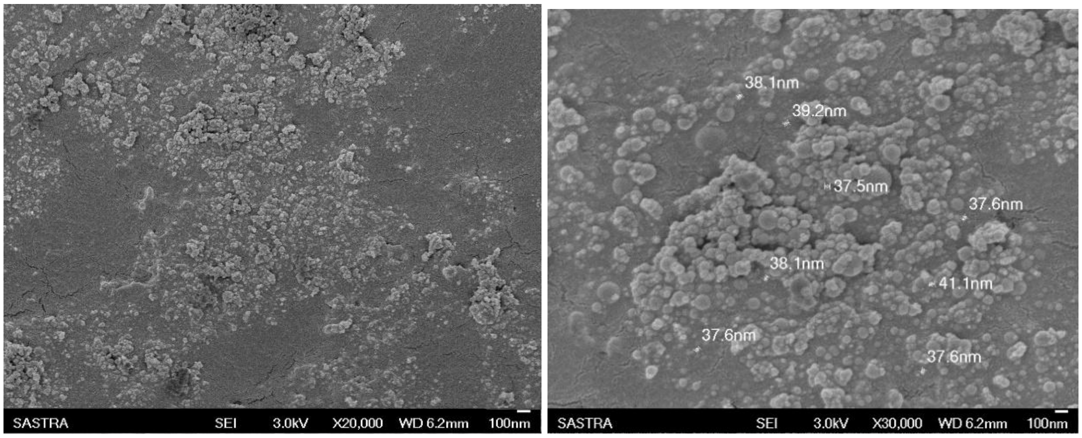


Fig. 2. SEM images at ~~20000x~~ X20,000 and ~~30000x~~ X30,000 magnification of Al_2O_3 NPs

Fig. 3

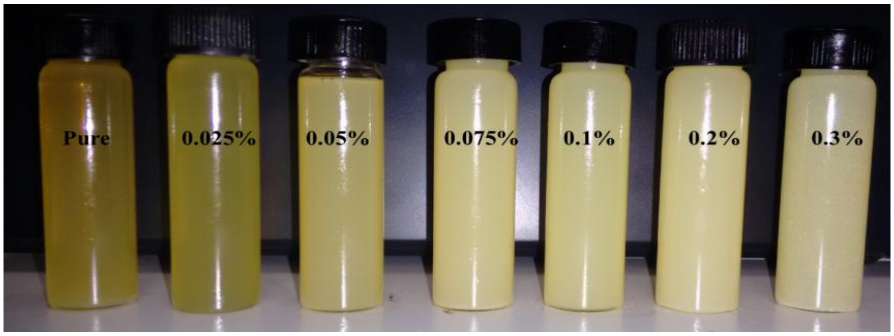


Fig. 3. nHTFs prepared using different volumetric concentrations of NPs

Fig. 4

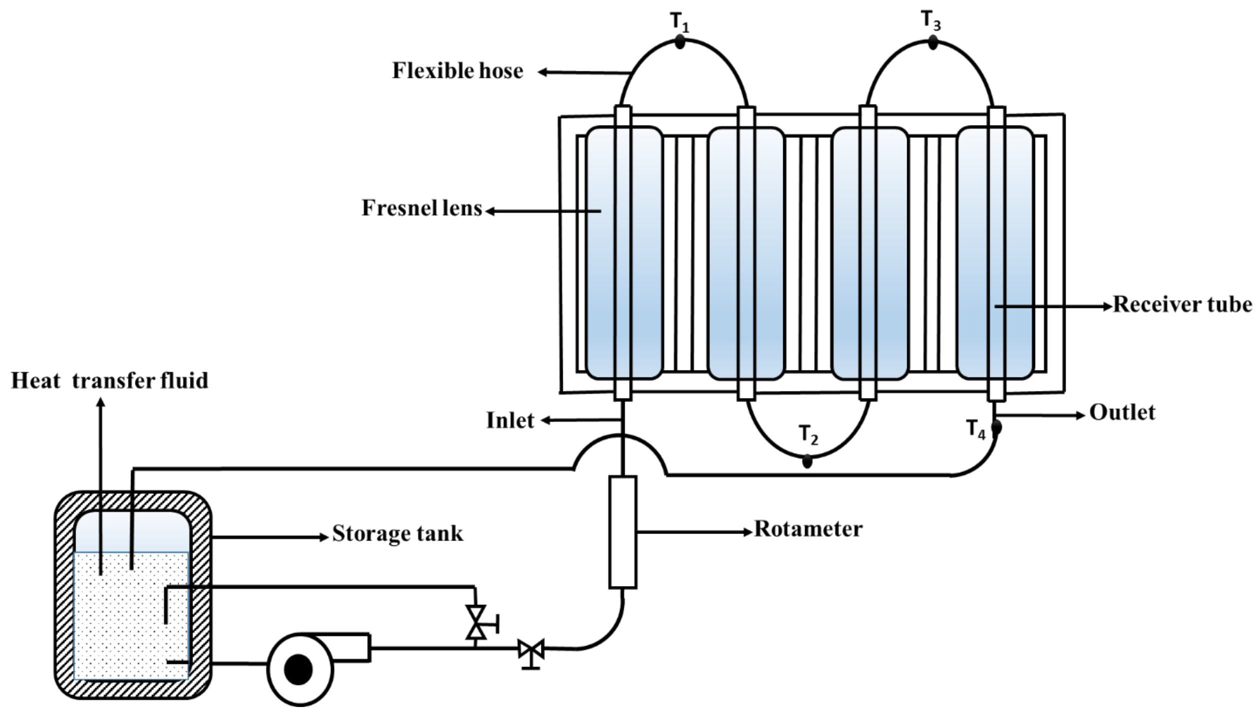
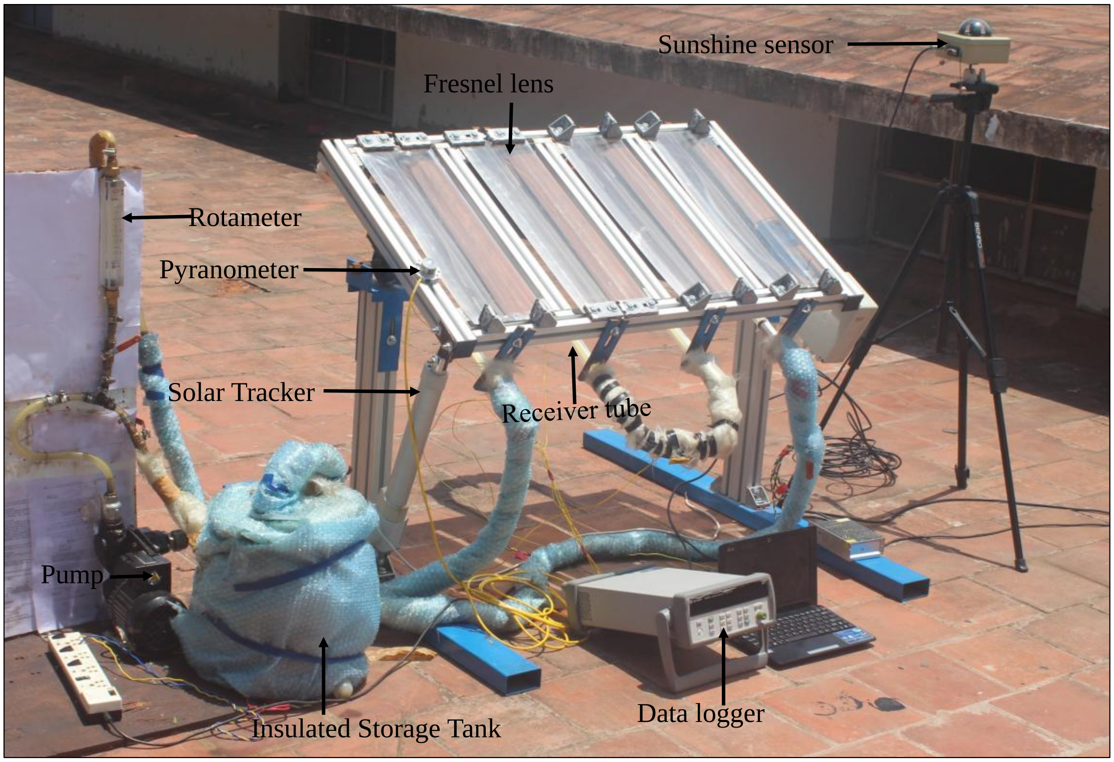


Fig. 4. Schematic diagram of the solar concentrator experimental test rig developed

Fig. 5



(a)

(b)

Fig. 5. (a) Fully instrumented solar concentrator under outdoor testing and (b) A receiver tube showing the illuminated directly absorbing nHTF

Fig. 6

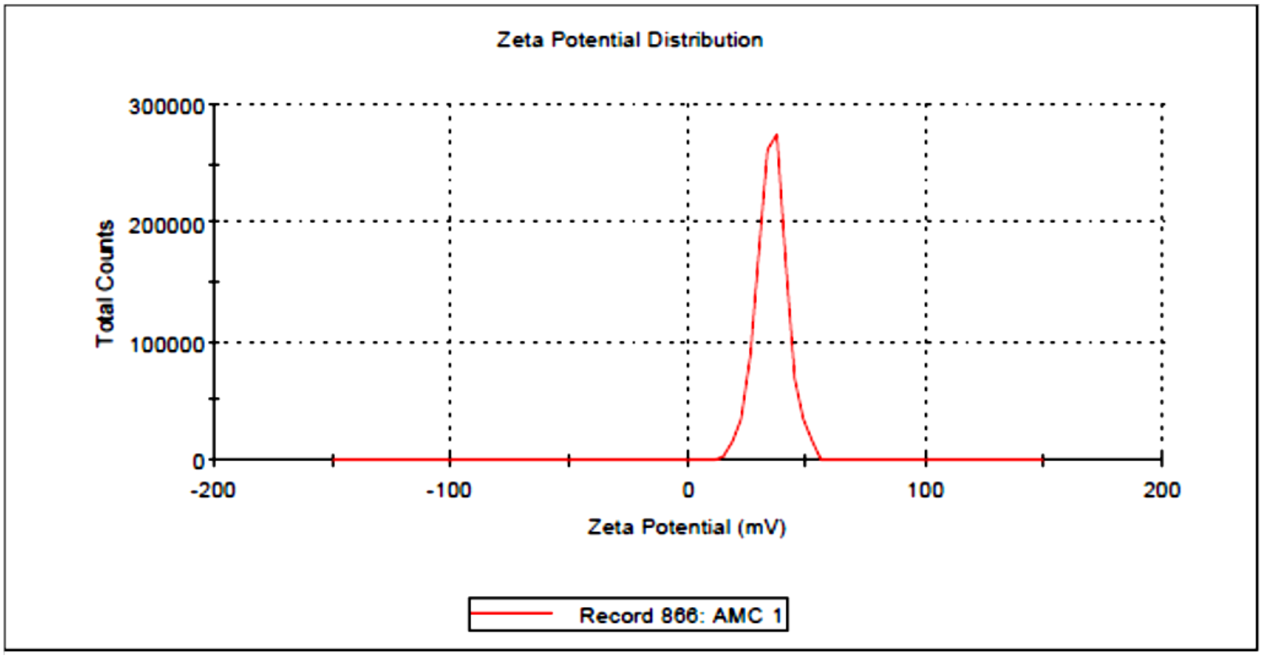


Fig. 6. Zeta potential distribution of the nHTF with 0.1 vol% Al_2O_3 in Therminol®55

Fig. 7

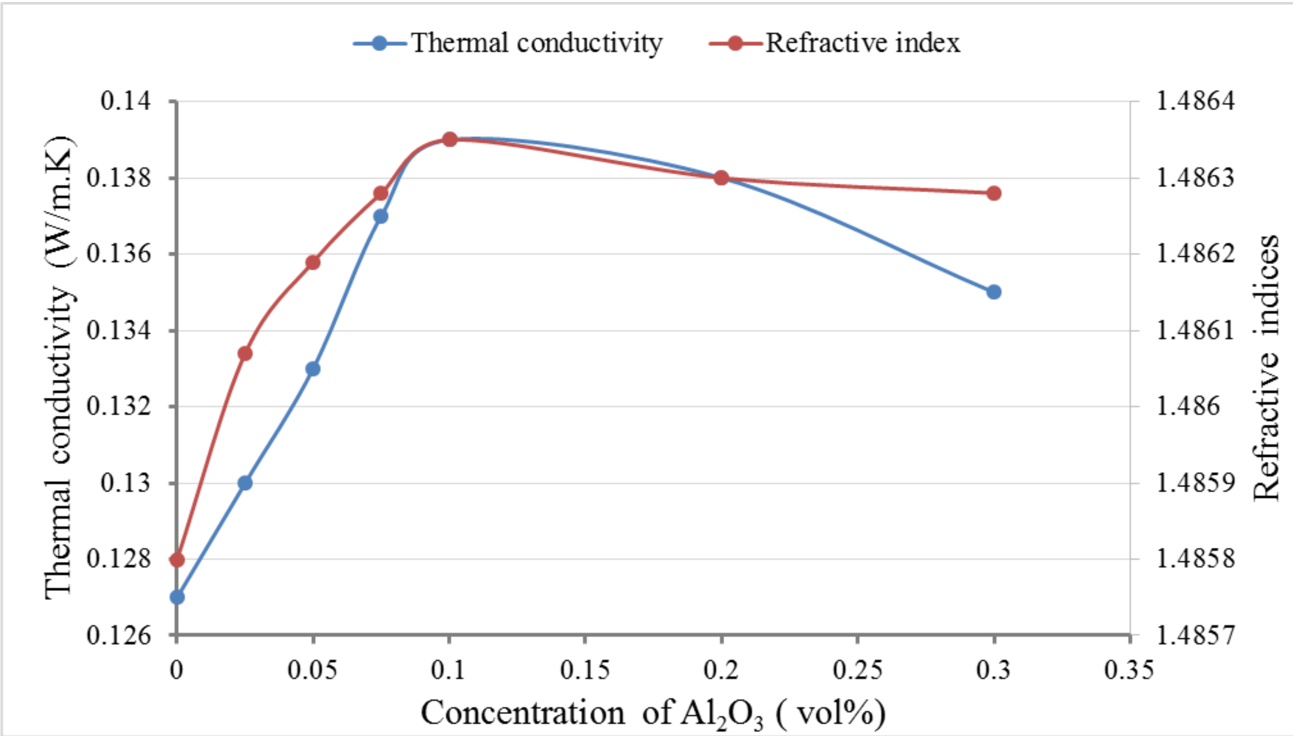


Fig. 7. Refractive indices and thermal conductivity of pure Therminol®55 and nHTF measured

Fig. 8

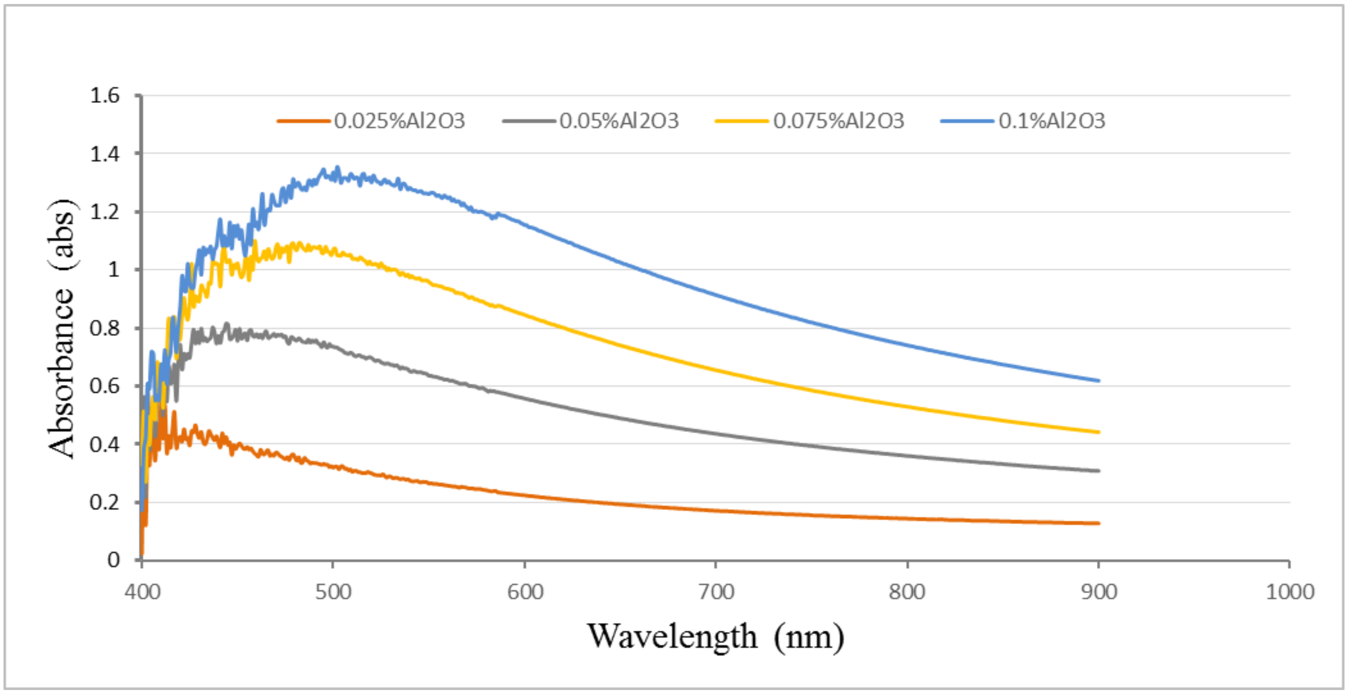


Fig. 8. Absorbance spectra of nHTFs measured during the study

Fig. 9

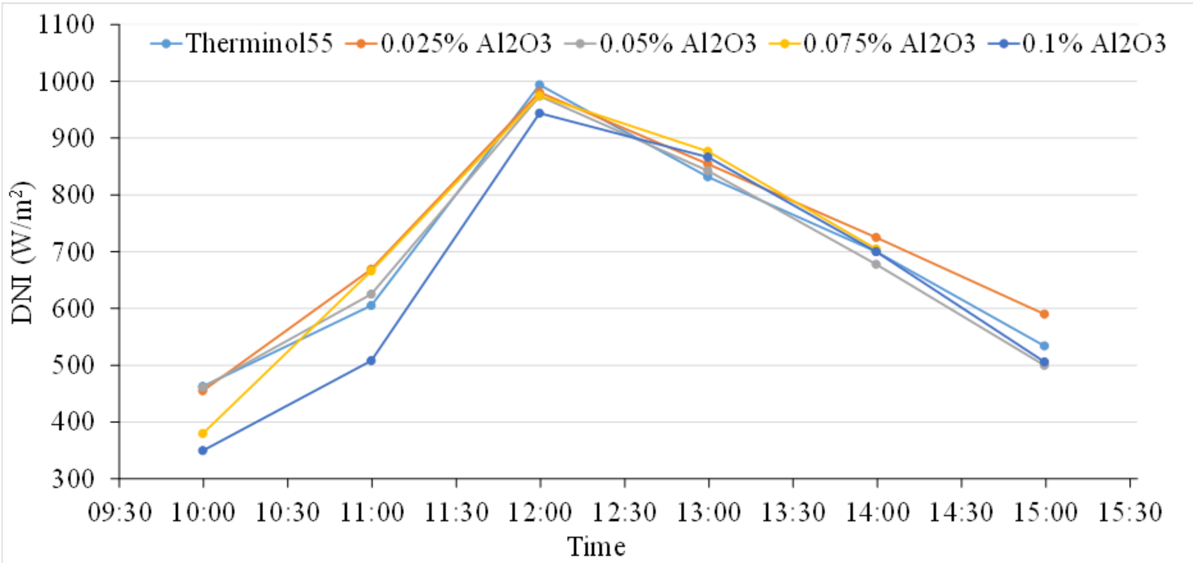


Fig. 9. DNI incident at inlet aperture of the Fresnel lenses during experiments

Fig. 10

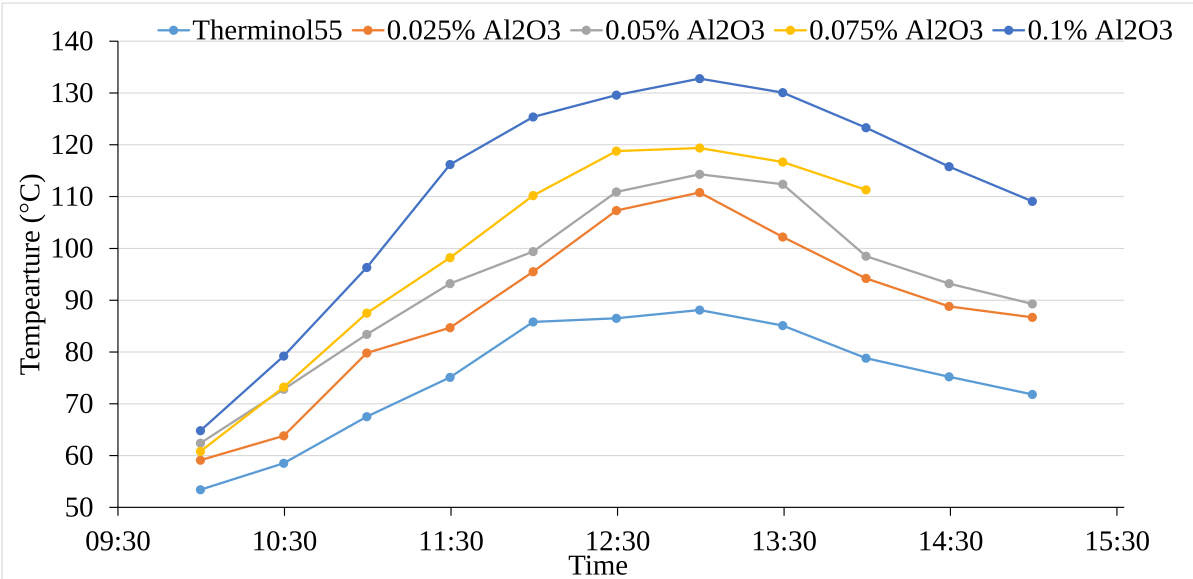


Fig. 10. Instantaneous half hourly temperatures of the nHTFs recorded at the outlet of the solar collector

Fig. 11

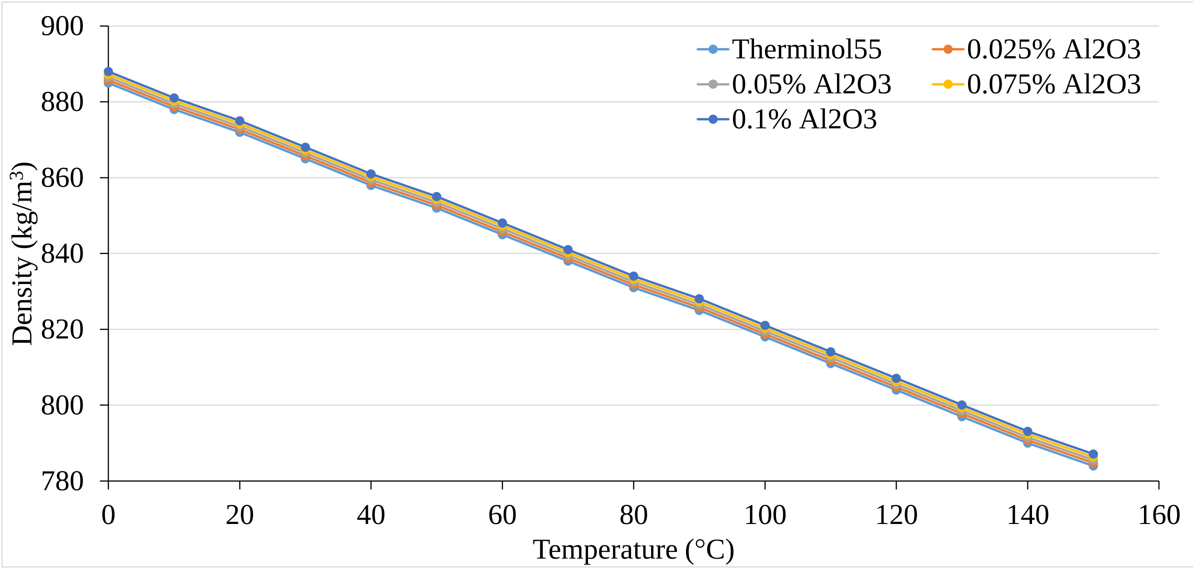


Fig.11. Density variation of nHTF with temperature and concentration of Al_2O_3 nanoparticles

Fig. 12

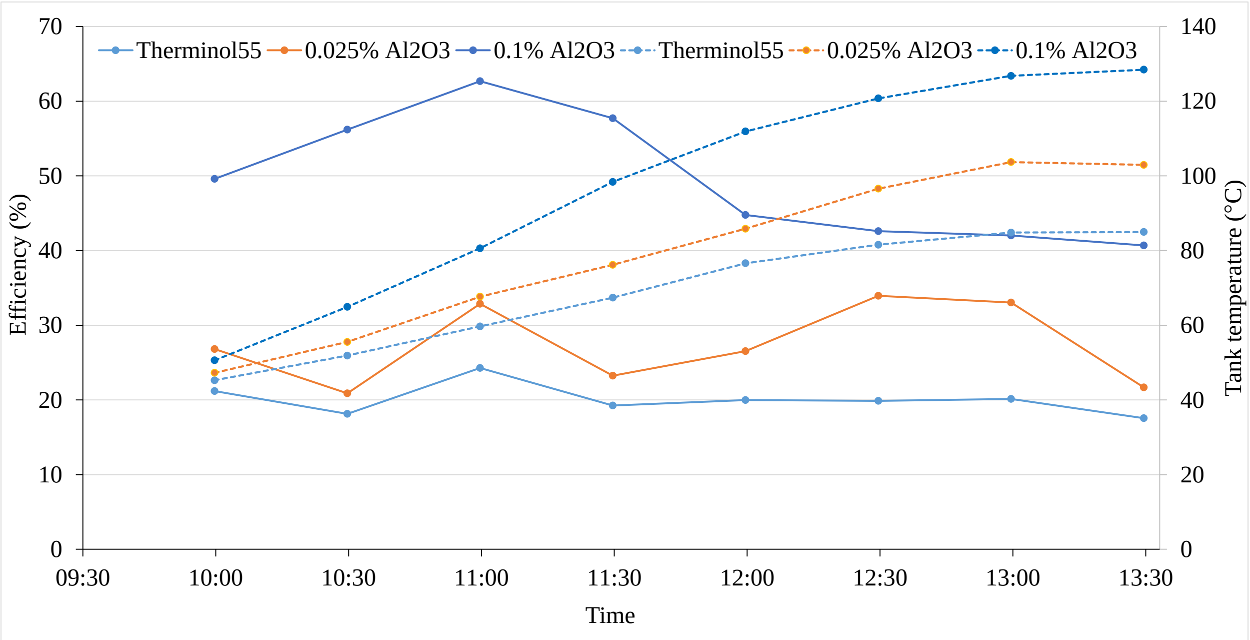


Fig. 12. Half-hourly solar collector efficiency (solid lines) and tank temperature (dotted lines)

Table 1

Table 1. Proportions of Alumina and Oleic acid in nHTF

Volume Concentration of Alumina (vol%)	Mass of Alumina (g)	Amount of Oleic acid (ml)
0.025	0.057	0.002
0.05	0.114	0.005
0.075	0.171	0.008
0.1	0.228	0.011
0.2	0.456	0.022
0.3	0.685	0.034

Table 2

Table 2. Selected specifications of characterization instruments employed

Instrument	Accuracy
KD2 PRO	Thermal conductivity ± 5 to ± 10%; Specific heat ± 10%; Thermal diffusivity ± 10%
Double Beam Spectrophotometer - (UV 3200)	± 0.1 nm @656.1 nm D2, ± 0.3nm (190 to 1100nm)
Rudolph Research - J257 refractometer	Refractive index ±0.00002, BRIX ±0.01
Zetasizer Nano ZS	0.12µm.cm/V.s
Pyranometer	Temperature response < -0.15 %
Thermocouples	± 0.5 °C

Table 3

Table 3. Specification of Fresnel lens and the receive tubes employed

Item	Specification
Fresnel Lens	Flat PMMA 250µm thick substrate film; Focal length 130 mm; Width 180 mm and Length 550 mm
Receiver tube	Glass in glass construction; internal diameter 10mm; Outer diameter 23mm; Evacuated length 550mm; Total length 700mm; Air pressure in the evacuated part 10^{-3} mbar

Table 4

Table. 4. Zeta potential values measured for the full range of nHTFs studied

Al_2O_3 concentration (vol%)	Zeta potential value (mV)
0.025	52.4
0.05	44.1
0.075	40.3
0.1	36.1
0.2	29.3
0.3	24.8

Table 5

Table 5. Specific heat (J/kg.K) of the nHTFs

Temperature (°C)	Therminol®55	Pure Al_2O_3	0.025 vol% Al_2O_3	0.05 vol% Al_2O_3	0.075 vol% Al_2O_3	0.1 vol% Al_2O_3
30	1940	880	1829.8	1829.5	1829.3	1829.1
40	1980	880	1869.8	1869.5	1869.3	1869.0
50	2010	880	1909.7	1909.5	1909.2	1909.0
60	2050	880	1939.7	1939.5	1939.2	1938.9
70	2080	880	1979.7	1979.5	1979.2	1978.9
80	2120	880	2009.7	2009.4	2009.2	2008.9
90	2160	880	2049.7	2049.4	2049.1	2048.8
100	2190	880	2079.7	2079.4	2079.1	2078.8
110	2230	880	2119.7	2119.4	2119.1	2118.8
120	2260	880	2159.7	2159.4	2159.0	2158.7
130	2300	880	2189.7	2189.3	2189.0	2188.7
140	2330	880	2229.7	2229.3	2229.0	2228.7
150	2370	880	2259.7	2259.3	2259.0	2258.6